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Procedia Environmental Sciences 18 (2013) 478 – 485

Procedia Environmental Sciences

2013 International Symposium on Environmental Science and Technology (2013 ISEST)

Photocatalytic Degradation of Methyl Orange with Commercial Organic Pigment Sensitized TiO_2

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Abstract

In this paper, TiO_2 photocatalyst sensitized with commercial organic pigment, C.I. Pigment Yellow 154 (PY) or C.I. Pigment Red 254 (PR) was prepared by solvothermal method, respectively. Photocatalytic activities of the as-prepared pigment/TiO_2 composites was evaluated by the degradation of the methyl orange (MO) under visible light irradiation. Microstructural, morphological, and optical properties of the as-prepared pigment/TiO_2 composites were characterized by X-ray diffraction technique (XRD), BET surface area analysis, UV–vis diffuse reflectance spectrum (UV–vis DRS). Results displayed that the as-prepared pigment/TiO_2 composites have high visible light photocatalytic activity and stability. The TOF of pigment/TiO_2 based on the content of pigment had nearly loss when the photocatalyst was used four times. The remarkable enhancement in the visible light photocatalytic activities of the pigment/TiO_2 heterostructures could be attributed to the effective electron–hole separations at the interfaces of the two semiconductors.

Keywords: Commercial organic pigment; Methyl orange; TiO_2; Photocatalysis; Visible light

1. Introduction

Titanium dioxide as a photocatalyst for mineralization of organic pollutants has attracted much attention because of its various advantages [1]. However, the large band–gap energy (3.2 eV) of TiO_2 considerably limits the utilization of natural solar light or artificial visible light [2]. As a surface modification technology, dye sensitization can be effective in broadening the range of semiconductor absorption [3, 4]. The properties of the dye play an important role in determining semiconductor photocatalytic performance. Due to the aqueous solubility of dye [5], the dye sensitized TiO_2 will easily

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doi:10.1016/j.proenv.2013.04.064

and frequently lose visible light activity in the course of photocatalytic degradation of organic pollutants[6].

In response to this defect, we selected special commercial stable pigment as sensitizer because of its high absorption coefficient within the solar spectrum and insoluble properties in water. C.I.Pigment Yellow 154 (PY) made in China, a commercial pigment with benzimidazolone azo group, is often used as automobile coatings because of its notable stability, weather resistance and solvent resistance. C.I.Pigment Red 254 (PR) is often used for printing inks, plastic, paint and coating because of its high colour strength, excellent heat and light resistance. Fig. 1 illustrates molecular structure of PY and PR. In this study, PY and PR sensitized TiO_2 (labelled as PY/TiO_2 and PR/TiO_2 respectively) photocatalysts were prepared by solvothermal method. The photocatalytic activity and stability of PY/TiO_2 were evaluated on the degradation of methyl orange (MO) under visible light irradiation.

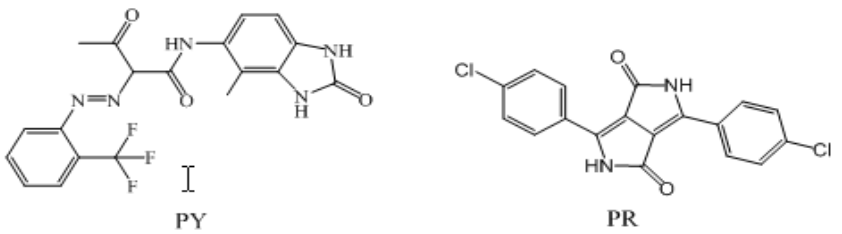

Fig. 1. Molecular structure of PY and PR.

2. Experimental

2.1. Materials and preparation of PY/TiO_2 and PR TiO_2

The modified TiO_2 with PY (PY/TiO2) was prepared by solvothermal method as follows. A mixture of PY (1.1 mmol), Span 80 (0.5 mmol) and DMF (80 mL) were sealed in a 100 mL Teflon–lined sealed reactor and heated in an oven at 150 °C. After 0.5 h the resultant mixture was filtered hot to remove trace amounts of insoluble solids and obtain solution A. 4.14 g TiO2 (P25, 51.8 mmol) was dispersed in approximately 20 mL of DMF under ultrasonic vibrations at room temperature for 10 min to obtain white slurry B. Solution A and slurry B were diverted into a 125 mL Teflon–lined sealed reactor and heated in an oven at 195 °C for 4 h, and then slowly cooled to room temperature. After filtration, the resulting powder was washed with distilled deionized water and ethanol several times and dried at 80 °C in oven to obtain a yellowish powder of PY/TiO2 photocatalyst (4.38 g), and proved that 54% of original PY was deposited onto TiO2. PR/TiO2 was prepared as the same method and the dosage of reactants were the same also, and 48% of original PR was deposited onto TiO2. The contents of organic pigment in catalysts (PY/TiO2 and PR/TiO2) are 5.5% and 4.4% for PY and PR respectively.

2.2. Characterizations of PY/TiO_2 and PR TiO_2

To determine the crystal phase composition of as-prepared photocatalysts, X–ray diffraction (XRD) measurements were carried out using a X'Pert Pro X–ray diffractometer (PANAalytical, Holland) with Cu Kα radiation, the diffractograms were recorded in the 2θ range 10°–80° with steps of 0.017°. The surface

physical morphology of the photocatalysts was measured by nitrogen adsorption isotherms at -196 °C by using a Micromeritics Tristar II 3020 system (Micromeritics Instrument Corporation, America). UV–Vis diffuse reflectance spectra were performed using a PerkinElmer Lambda 750 spectrophotometer (Perkin Elmer Corporation, America).

2.3. Measurements of adsorption capacities and photocatalytic activities

The experiments were carried out in a custom-made adsorption-photodegradation reactor. The reactor consists of a 120 mL Pyrex glass bottle with a jacket outside and a 150 W tungsten iodine lamp in parallel to the reactor. To ensure the experiments were carried out under visible light, the light beam was passed through optical filter (JB420, Jiangsu Haian Education Optical Lens Factory, China) to cut-off wavelengths shorter than 420 nm. The photocatalytic activity of the as-prepared photocatalysts was evaluated by degradation of MO. Reaction suspensions were prepared by adding different photocatalysts to 100 mL MO solution (Initial concentration: 8.3×10^{-5} mol/L, catalyst dose 0.6 g/L) under vigorous stirring. The samples were collected at regular intervals of time and analyzed by Agilent 8453 UV–Vis spectrometer to measure the temporal changes of solution concentration. The concentration of MO was calculated by its calibration curve.

3. Results and discussion

3.1. Characterization of photocatalysts

3.1.1. XRD patterns

The XRD patterns of the original TiO_2, PR/TiO_2 and PY/TiO_2 are shown in Fig. 2 The original TiO_2 exhibits typical patterns that can be well indexed to the phases of anatase and rutile. The modification of TiO_2 by pigment PY or PR does not cause obvious change in their peak positions and shapes compared with the original TiO_2, which indicating that the sensitization of TiO_2 through solvothermal treatment has not changed the crystalline structure of original TiO_2.

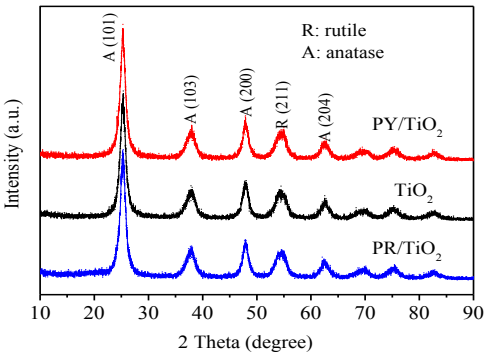

Fig. 2. XRD patterns of TiO_2, PY/TiO_2 and PR/TiO_2.

3.1.2. N2 Adsorption

The specific surface areas, average pore size and pore volume of the original TiO_2 and as-prepared

photocatalysts were characterized using the N_2 adsorption technique. Fig. 3 shows the N_2 adsorption-desorption isotherms for PY/TiO_2, PR/ TiO_2 and TiO_2. Table 1 summarizes their physical properties. The TiO_2 modified by PY or PR are aggregated to some extent during solvothermal treatment, leading to a marked decrease of the *BET* surface areas and the pore volume, and a marked increasing of the average pore size.

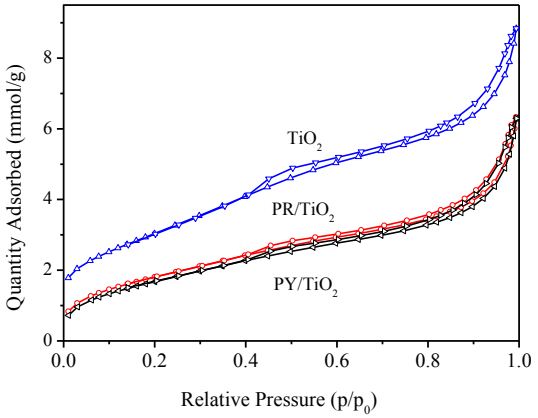

Fig. 3. N_2 adsorption and desorption isotherms of TiO_2, PR/TiO_2 and PY/TiO_2.

Table 1. Structural characteristic of TiO_2 and PY/TiO_2 .

	Specific surface area (m^2/g)	Pore volume (cm^3/g)		Pore size (nm)	
	S_{BET}	$V_{BJH\text{-}A}$	$V_{BJH\text{-}D}$	$PS_{BJH\text{-}A}$	$PS_{BJH\text{-}D}$
TiO_2	21.85	0.3314	0.3293	51.23	49.53
PY/TiO_2	14.77	0.2304	0.2297	62.29	60.8
PRTiO_2	14.34	0.2333	0.2325	60.23	58.96

S_{BET} = BET surface area;

$V_{BJH\text{-}A}$ = BJH adsorption cumulative volume of pores;

$V_{BJH\text{-}D}$ = BJH desorption cumulative volume of pores between 17 nm and 3000 nm width;

$PS_{BJH\text{-}A}$ = BJH adsorption average pore size; $PS_{BJH\text{-}D}$ = BJH desorption average pore size.

3.1.3. UV–Vis diffuse reflectance spectra

Fig. 4 shows the UV–Vis diffuse reflectance spectra (UV–vis DRS) of PY/TiO_2, PR/TiO_2 and original TiO_2. Obviously, there was no absorption above 400 nm for pure TiO_2, while PY/TiO_2 and PR/TiO_2 show clear visible light absorption from 400 to 600 nm. Approximately, the absorption edges of original TiO_2, PY/TiO_2 and PR/TiO_2 are located at 382, 529 and 610 nm in the near-UV and visible light regions, respectively.

The reduction in the band gap energy of the as-prepared sample was determined by the following equation [7]:

$$Eg = \frac{1240}{\lambda} \quad (1)$$

where Eg is the band gap energy (eV) and λ is the wavelength (nm) of the absorption edge in the spectrum. Accordingly, the band gap of PY and PR are evaluated to be 2.34 eV and 2.03 eV, hence they can be excited by visible light (λ>400 nm, Eg<3.1 eV), whereas the band gap of TiO_2 is found to be about 3.25 eV.

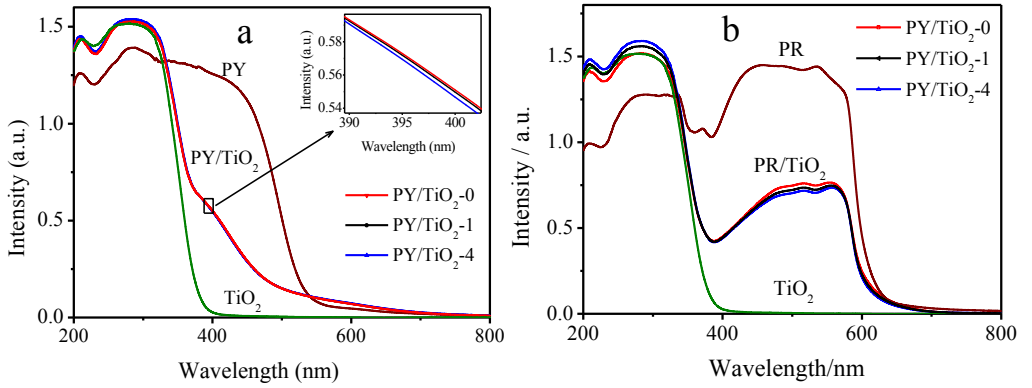

Fig. 4. UV–Vis diffuse reflectance spectra. (a) PY, PY/TiO_2 and TiO_2; (b) PR, PR/TiO_2 and TiO_2. -0, -1,-4 are the number of cycle of the catalyst used for photocatalytic experiment.

3.2. Photocatalytic activity

MO, a stable acid azo dye, is a compound that contain azo groups (–N=N–) linked to aromatic sp^2–hybridized C–atoms. MO is commonly used as titration indicator and staining agent in view of its high stability. In this paper, we investigated the photocatalytic activity of the prepared photocatalyst on the degradation of MO.

Fig. 5 shows UV–Vis spectral changes of MO aqueous solution in the presence of PY/TiO_2. Photocatalytic reaction started after 65 min of adsorption in the dark, the adsorption equilibrium had been established. The peak wavelength of MO aqueous solution clearly blue–shifted to the shorter range and simultaneously broaden under visible light irradiation, which is caused by *N*-demethylation according with the study reported by Zhu et al. [8], Han et al. [9] and Zhu et al. [10].

The changes in the concentration of MO aqueous solution under visible light irradiation in the presence of different photocatalysts are illustrated in Fig. 6 The degradation rate reached 89.2% and 50.9% respectively in 195 min. It is notable that PY/TiO_2 and PR/TiO_2 showed higher photocatalytic activities than pure TiO_2.

3.3. Turnover frequency (TOF) and recycle ability of the catalyst

The catalyst turnover number (*TON*) and the turnover frequency (*TOF*) are two important quantities used for comparing catalyst efficiency. In heterogeneous catalysis, the *TON* is the number of reactant molecules that is converted into products in presence of 1 g of catalyst [11]. The *TOF* is simply *TON*/time. For pigment/TiO_2 catalyst using MO solution (Initial concentration: 27 mg/L) and 0.6 g/L catalyst dose, the *TOF* based on the content of pigment were found to be 5.9×10^{-7} and 3.8×10^{-7}molecules/g/min for the first cycle for PY/TiO_2 and PR/TiO_2 respectively.

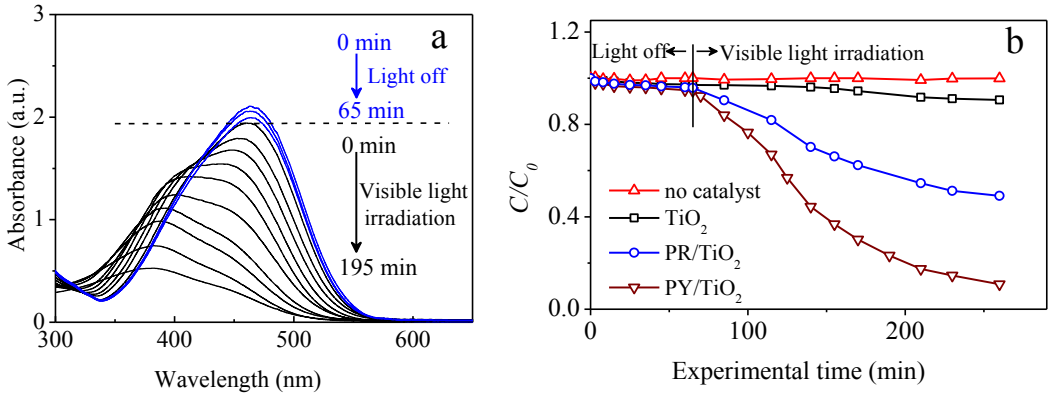

Fig. 5. (a) Temporal spectral changes of MO in aqueous PY/TiO_2 suspensions under visible light irradiation,;(b) Photodegradation of MO under different photocatalysts.

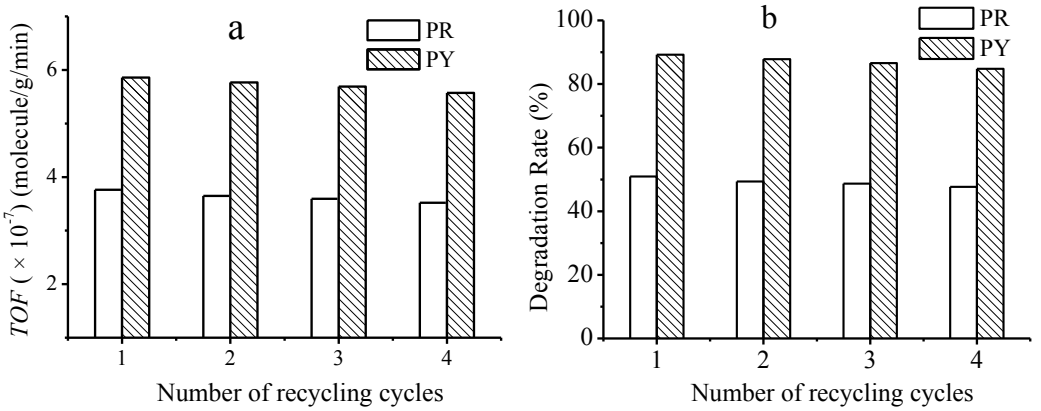

Fig. 6. (a) *TOF*, and (b) MO photodegradation at successive catalytic cycles. Concentration of MO: 27 mg/L; Catalyst dose: 0.6 g/L; Irradiation time: 195 min.

To make the process cost-effective and greener, the recycle ability of pigment/TiO_2 was evaluated. After completion of one catalytic cycle, the used photocatalyst was collected by filtrating the suspension and washed with distilled deionized water to remove the bulk solution, dried in oven at 100 °C for 0.5 h. There is little loss of photocatalytic activity observed when the photocatalyst was used four times (Fig. 6), which illustrate that the content of pigment in catalyst has nearly change, and this can also be proved by the UV–vis DRS spectra (Fig. 4). This excellent chemical and mechanical stability of as prepared photocatalyst were critical properties for industrial application in the near future. The immobilization of such pigment sensitized organic-inorganic hybrid photocatalyst is undergoing further investigation in our lab.

3.4. Possible photocatalytic mechanism

To the best of our knowledge, efficient photoinduced electron–hole separation and transfer are the key

factors to a photocatalytic reaction; hence it is important and necessary to inhibit the recombination of photoinduced carriers [12]. On the basis of the above experimental studies, a schematic diagram of the band levels of the pigment/TiO_2 composites and the possible reaction mechanism of the photocatalytic procedure are proposed and illustrated in Fig. 7 .

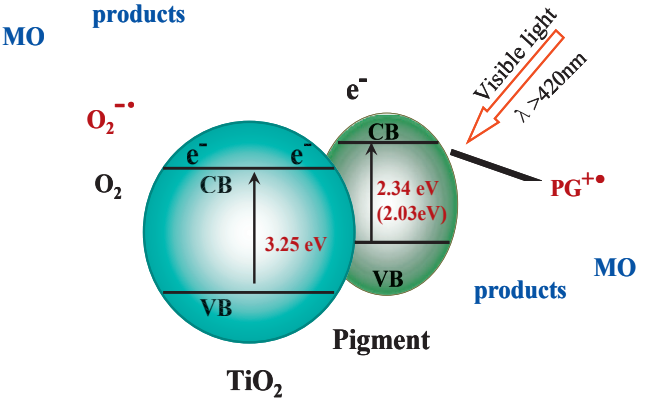

Fig. 7. Schematic diagram of the band levels of pigment/TiO_2 composites and the possible reaction mechanism of the photocatalytic procedure.

Pigment has so narrow band gap energy that it could be irritated easily by visible light and consequently induces the generation of photoelectrons and holes. In fact, pure pigment has poor photoactivity because its narrow band gap energy would result in rapidly recombined for photoelectrons and holes. Meanwhile, TiO_2 possesses both strong electron affinity and high electron conductivity but with a wide energy gap of 3.25 eV, thus it could not be excited by the visible-light irradiation. However, in the case of pigment/TiO_2 heterostructures, we can observe that when pigment are illuminated by photon energy less than 2.95 eV (λ > 420 nm), the photoinduced electrons in the reformed conduction band (CB) potential edge on the surface of pigment could easily flow to a lower CB potential edge of TiO_2 [13], thus the recombination of photogenerated electron–hole pairs could be effectively inhibited and the corresponding photocatalytic properties would be greatly improved.

4. Conclusions

This work has shown that the commercial stable pigment (PY and PR) sensitized TiO_2 displaying high visible light photocatalytic activity than original TiO_2 on the degradation of MO. The *TOF* of catalyst for MO based on the content of pigment has nearly loss during the cycle experiment. UV–vis DRS spectra confirmed that the modified catalyst absorbed more photons under visible light irradiation. The research work done thus far suggest that TiO_2 sensitized with small amounts of specific pigment to construct stable organic-inorganic hybrid photocatalytic systems in the heterogeneous photodegradation of organic pollutants has a potential application in wastewater treatment by using solar light or artificial visible light.

Acknowledgements

This work was supported by National Natural Science Foundation of China (21103121&21276027), the Doctoral Fund of Ministry of Education of China (20110032120011) and Project of Shandong Province Higher Educational Science and Technology Program (J12L64).

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